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13. ABSTRACT (Maximum 200 words) An excimer laser system capable of producing high-intensity laser radiation in the ultraviolet spectra region has been acquired and is being used for studies of the spectroscopy and collision dynamics of a number of important transient molecular species of importance in the flame chemistry of potential fire suppressant agents. In particular, the excimer laser was employed for the photolytic preparation of transient species of interest. Spectroscopic investigations of several iron-containing molecules, including FeCl, FeO, and FeNC, have been carried out. A study of collisional electronic quenching and vibrational energy transfer of the excited CF($A^2\Sigma^+$) molecule in collisions with a number of atomic and molecular colliders has been carried out. The electronic spectroscopy of the PO ₂ radical, prepared in a rotationally cold supersonic beam, has also been investigated.					
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**DURIP00: SPECTROSCOPIC CHARACTERIZATION
OF FREE RADICAL INTERMEDIATES**

FINAL REPORT

Paul J. Dagdigian

The Johns Hopkins University

Army Research Office

Grant Number DAAD19-00-1-0022

ITEMIZATION OF EQUIPMENT PURCHASED

The funds awarded under grant no. DAAD19-00-1-0022 were used to acquire an excimer laser system capable of producing high-power pulsed ultraviolet radiation and associated monitoring electronics.

The following specific items, with the manufacturer and costs, were acquired with funds from this grant

(1)	Compex 102 excimer laser, multigas version	\$55,530
	Lambda Physik, Fort Lauderdale, FL	
(2)	Regulators for excimer gases: one fluorine regulator	2,117
	with cross purge and filter and two high-purity	
	inert gas regulators	
	Spectra Gases Inc., West Branchburg, NJ	
(3)	Model LT732 digital oscilloscope	6,711
	LeCroy, Chestnut Ridge, NY	
(4)	Model SRS250 gated integrator	2,996
	Stanford Research Systems, Sunnyvale, CA	
(5)	Model 555-3 digital delay generator	3,490
	Berkeley Nucleonics Corp., San Fafael, CA	
(6)	Movable table to support excimer laser	1,184
	Chemistry Department machine shop	

The cost of item 5 was shared with another revenue source so that the total amount charged to this grant and the associated Johns Hopkins cost sharing totaled \$70,000.

SUMMARY OF RESEARCH ACCOMPLISHED

The equipment acquired under grant no. DAAD19-00-1-0022 is being used in the projects described below. Supported by ARO grant no. DAAG55-98-1-0312, we have been investigating the spectroscopy and dynamics of important transient species in the flame chemistry of compounds with fire suppression propensities. These experiments have been greatly facilitated by the availability of the excimer laser and associated electronics acquired through the present instrumentation grant. Excimer laser photolysis provides a particularly convenient method for the generation of the transient species of interest. These intermediates have been generated in jet-cooled molecular beams for spectroscopic studies or in cells for measurement of quenching and energy transfer rate constants.

There is a critical need for new, environmental acceptable fire suppressants, because of the ongoing phaseout of halons. However, an agent with all the desirable properties is proving difficult to identify.¹ Some metal-containing compounds have been found to be very effective flame inhibitors. In particular, $\text{Fe}(\text{CO})_5$ has been found to be an especially strong inhibitor and at low concentrations very effectively reduces the flame velocity in methane/oxygen flames.² While the toxicity of $\text{Fe}(\text{CO})_5$ prevents its use as a fire suppressant, nevertheless a detailed understanding of its effect upon flame chemistry would be very helpful in developing new fire suppressant agents. Kinetic modeling of suppressed CH_4/air flames yields results similar to those observed in the laboratory and strongly suggests that a homogeneous mechanism involving a reduction in the H atom concentration is responsible for the inhibition. Skaggs *et al.*³ reported the first measurements of a radical species (OH) in a low-pressure, nonpremixed flame as a function of added $\text{Fe}(\text{CO})_5$.

It would be desirable to measure the concentrations of Fe-containing species in such flames. In ARO-supported work carried out prior to the acquisition of the excimer laser system, we investigated the collisional quenching and electronic energy transfer of excited Fe atoms.⁴ The collisional behavior of electronically excited transition metal

atoms has been relatively unexplored. We believe that the $z^5D^0 \leftarrow a^5D$ multiplet near 372 nm is the most suitable for the measurement of Fe atom concentrations in a flame, since this is the longest-wavelength transition whose upper level has a sub- μ s lifetime. Accordingly, we have measured electronic quenching and energy transfer rate constants for the multiplet levels of the excited z^5D^0 state.

1. *Electronic Spectroscopy of Iron-Containing Molecules*

In addition to spectroscopic probes of Fe atom concentrations, discussed above, it is also important to have probes of Fe-containing species. Progress in unraveling the electronic spectra of iron-containing molecules has been slow because of the extreme spectral complexity and congestion. We have been able to extend the spectroscopy of two diatomic iron-containing molecules and to observe spectroscopically for the first time a triatomic iron-containing molecule. There are two types of low-lying electronic transitions which can occur in a transition-metal compound: a valence transition (metal $d - d$ or charge transfer) or a metal-centered $4p \leftarrow 4s$ transition. Our studies of the FeCl and FeNC molecules exemplify the latter, while the orange band system of FeO typifies the former.

(a) *The FeCl Molecule.* We have carried out a molecular beam study of the ${}^6\Pi - X^6\Delta$ band system of FeCl, whose origin band lies near 357 nm.⁵ FeCl was prepared in a pulsed supersonic free-jet expansion by reaction of 193 nm photolyzed $\text{Fe}(\text{CO})_5$ and CCl_4 diluted in Ar. We have observed the $\Delta v = 1, 0, -1, -2$ sequences and have detected vibrationally excited FeCl ($v'' \leq 4$) for the first time. Assignment of the spectrum was greatly facilitated by the low rotational temperature of the FeCl in the supersonic beam.

The ${}^6\Pi_{\Omega'} = \Omega'' - 1 - X^6\Delta_{\Omega''}$ subbands for $\Omega'' = 9/2, 7/2$, and $5/2$ were observed and were found to have regular rotational structure. Of the three other subbands ($\Omega'' = 3/2, 1/2$, and $-1/2$), only the ${}^6\Pi_{1/2} - X^6\Delta_{3/2} (0,0)$ subband could be assigned. This subband exhibited a very large Λ doubling, indicative of mixing of the excited fine-structure level with neighboring electronic states. With our observations and the previous⁶ observation of a ${}^6\Phi - X^6\Delta$ band system lying to slightly shorter wavelength, it was possible to derive

parameters describing the diagonal and off-diagonal electrostatic + spin-orbit matrix elements⁷ of the sextet electronic states associated with the $4p \leftarrow 4s$ transition in FeCl.⁵

(b) *The FeO Molecule.* The FeO orange band system has been known for a long time, but the complexity of this system has considerably inhibited progress in its analysis.⁸ The ground electronic state is now known to have $^5\Delta$ symmetry. Merer and co-workers^{9, 10} concluded that the orange bands were consistent with the presence of two $^5\Delta \leftarrow ^5\Delta$ transitions, involving nominal electron promotions $3d\sigma \leftarrow 4s\sigma$ [$D^5\Delta \leftarrow X^5\Delta$] and $\text{Fe}(3d\pi) \leftarrow \text{O}(2p\pi)$ charge transfer [$D^5\Delta \leftarrow X^5\Delta$]. The radiative lifetimes were found to fall in the range 260 – 590 ns.¹¹

We have carried out a molecular beam study of the FeO orange bands over the 540 – 595 nm spectral region.¹² FeO was prepared in a pulsed supersonic free-jet expansion by reaction of 193 nm photolyzed $\text{Fe}(\text{CO})_5$ and N_2O diluted in Ar. All observed bands were found to be parallel polarized, with $\Delta\Omega = 0$, and involved transitions out of $\Omega'' = 4$ and 3 fine-structure levels. With the help of ground-state combination differences, it was possible to show that many of the observed bands involved excitation out of excited vibrational levels $v'' = 1 - 3$.

Our observation of numerous FeO hot bands provides Franck-Condon access to higher vibronic levels than previously observed. The previously observed^{9, 10} irregular pattern of vibronic energies persists to higher excitation energies, and only a few new vibrational assignments could be made. Several very strong bands in FeO flame spectra remain unassigned. In addition to the Fe-centered promotion and charge transfer excitation mentioned above, charge-transfer bands involving excitation of an electron out of the $\text{O}(2p\sigma)$ orbital are also possible. The presence of these strong unidentified bands suggests that there could be such electric-dipole allowed transitions in this energy range, in addition to the previously identified $D - X$ and $D' - X$ transitions.

(c) *The FeNC Molecule.* We have observed the first electronic spectrum of an iron-containing triatomic molecule, namely FeNC.¹³ This is also the first spectroscopic observation of a transition-metal cyanide/isocyanide molecule. There has been

considerable interest in the structure of MCN molecules because of the similar energetics of the cyanide and isocyanide structures.

The FeNC molecule was prepared in a pulsed supersonic free-jet expansion by reaction of 193 nm photolyzed $\text{Fe}(\text{CO})_5$ and CH_3CN diluted in Ar. A total of three bands, comprising an excited-state Fe–N stretch vibrational progression was observed in the spectral range 340 – 372 nm. The assignment of the molecular carrier and an estimation of the vibrationally averaged geometry was obtained by rotational analysis of FeN^{12}C and FeN^{13}C bands. Resolved fluorescence emission spectra were recorded.

All the observed bands involved $\Omega' = 7/2 \leftarrow \Omega'' = 9/2$ transitions, exactly analogous to the ${}^6\Pi_{7/2} - X^6\Delta_{9/2}$ subbands of the iron monohalides. This is consistent with the expected electronic structure of FeNC since the CN moiety behaves like a halogen atom. We can assign the observed electronic transition as an iron-centered $4p \leftarrow 4s$ excitation, in analogy with the near uv bands of the iron monohalides. Since both the ground and excited electronic state display large spin-orbit splittings, the equilibrium geometries in both states are linear.

2. Collisional Quenching and Energy Transfer in the CF Radical

We have carried out a study of collisional quenching and vibrational energy transfer of the $A^2\Sigma^+$ electronic state of the CF radical. This radical is an important transient intermediate in the chemistry of flames containing fluorinated hydrocarbons.¹⁴ It also occurs in plasmas which are used for etching SiO_2 layers in the fabrication of microelectronic circuits and plasmas which employ CF_4 and other partially or fully fluorinated hydrocarbons. The CF radical is conveniently detected by its $A^2\Sigma^+ - X^2\Pi$ electronic transition, whose origin band lies near 233 nm. Only the $v' = 0$ and 1 vibrational levels decay radiatively.¹⁵

To our knowledge, collisional quenching rate constants have not been previously determined for the $\text{CF}(A^2\Sigma^+)$ electronic state. We have measured rate constants for electronic quenching of the $v' = 0$ and 1 vibrational levels of $\text{CF}(A^2\Sigma^+)$ with a number of colliders.¹⁶ Quenching could not be detected for He and Ar. The rate constants were

somewhat larger for $v' = 1$ than for $v' = 0$. The largest rate constants were found for C_3H_8 , CH_4 , and O_2 colliders $[(25 - 68) \times 10^{-10} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ for $v' = 0]$. Surprisingly, quenching by CF_4 could not be detected. The $CF(A^2\Sigma^+)$ quenching rate constants are found to have a similar ordering of values as the quenching rate constants for the isovalent $CH(A^2\Delta)$ radical.

Spectrally resolved emission spectra were recorded in order to search for $v' = 1 \rightarrow v' = 0$ vibrational energy transfer (VET). Only in the case of the CH_4 collider was collisional vibrational energy transfer detected, and the VET rate constant was determined to equal $3.3 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$, corresponding to $\sim 1/4$ of the $v' = 1$ quenching rate constant.

3. *The Electronic Spectrum of the PO₂ Molecule*

Phosphorus-containing compounds have been proposed as potential fire suppressant agents. Dimethyl methyl phosphonate and trimethyl phosphate have been found to be significant inhibitors of nonpremixed methane-air flames.¹⁷ Phosphorus oxidation is fairly complicated.^{18, 19} One of the key intermediates is the PO_2 molecule, but spectroscopic information on this species is fairly sparse, in contrast to the extensive information available on the diatomic PO radical.²⁰

The electronic spectrum of PO_2 was first observed in a flash photolysis study.²¹ Several progressions of bands were observed in the region 312 – 268 nm. The laser fluorescence excitation spectrum of PO_2 was later reported by Hamilton,²² who also measured excited-state lifetimes and collisional quenching rates. In both these studies, the rotational structure was not resolved. High-resolution studies of pure vibrational transitions in PO_2 have been reported.²³

There have been a number of theoretical studies of the electronic states of the PO_2 radical. The most thorough and highest quality of these calculations was by Buenker and co-workers,²⁴ who computed the equilibrium geometries and vibrational frequencies of the low-lying electronic states and estimated vertical excitation energies and oscillator

strengths for the 18 lowest electronic states. Thus far, a definitive assignment of the excited state of the observed transition has not been made.

We have carried out a spectroscopic study of the PO_2 radical.²⁵ This species was prepared rotationally cold in a free-jet supersonic beam by the 193 nm photolysis of PCl_3 in the presence of O_2 diluted in an inert gas. We have observed the previously reported²¹ bands in the uv electronic band system, as well as many new bands. We have also recorded resolved emission spectra. With these observations, we have been able to extend the previous vibrational analyses^{21, 22} of both the ground and excited electronic states.

We have also recorded high-resolution scans of many of the observed bands. The rotational structure of the bands was found to be complicated and defied a detailed analysis. The calculations of Buenker and co-workers²⁴ offer two possibilities for the identity of the excited electronic state of the observed transition.

We also recorded fluorescence decay waveforms for excitation of many of the excited vibronic levels. In all cases, the decays were found to be nonexponential and were fitted with a double exponential form. The derived lifetimes for excitation of different rotational features within a given band were found to be significantly different. We also found that our measured lifetimes were significantly shorter than those reported by Hamilton,²² who prepared the radicals at room temperature in a cell. This suggests that there is strong dependence of the decay lifetime upon the degree of rotational excitation. We believe that the unanalyzable rotational structure of the bands and the inferred rotational dependence of the decay lifetimes implies significant mixing of the excited electronic state with the ground \tilde{X}^2A_1 state, as in the isovalent NO_2 molecule.²⁶ At the energy of the upper level of the electronic transition, the ground state of PO_2 is bound and can mix with the excited electronic state.

Research Publications Acknowledging ARO Grant No. DAAD19-00-1-0022.

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